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## DETAILED DESCRIPTION

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### [Detailed Description of the Invention]

[0001]

[Field of the Invention]In detail this invention to the proton (hydrogen ion) conductivity film which was rich in flexibility, its manufacturing method and the fuel cell using it, and a pan, In order to show the proton conductivity which was excellent in heat resistance or endurance and was moreover excellent also in the elevated temperature and to satisfy the various physical properties of mechanical performance like flexibility, It is related with the proton conductive film with which the direct fuel type fuel cell which supplies fuel, such as direct methanol and methane, can be presented, its manufacturing method, and the fuel cell using these proton conductive films further.

[0002]

[Description of the Prior Art]In recent years, since generation efficiency is highly excellent in environment nature, the fuel cell attracts attention as a power plant of the next generation which can contribute to solution of the environmental problem and energy problems which are big technical problems socially. Although a fuel cell is generally classified into some types according to an electrolytic kind, even if it compares a polymer electrolyte fuel cell (it may be hereafter called PEFC for short) with which other types, they are small size and high power also in this.

a small-scale type on site and a mobile (for example, power source of vehicles) -- it is considered as the next-generation main force as fuel cells, such as business and portable. Thus, PEFC has the outstanding strong point theoretically. Development towards utilization is performed briskly.

[0003]By the way, in this PEFC, hydrogen is usually used as fuel. Hydrogen is decomposed into a proton (hydrogen ion) and an electron by the catalyst installed in the anode side of

PEFC. Among these, an electron is supplied outside, and is used as electrical and electric equipment, and it circulates through it to the cathode side of PEFC. On the other hand, a proton is supplied to a proton conductive film (electrolyte membrane), and moves to the cathode side through a proton conductive film. In the cathode side, a proton, the electron through which it has circulated, and the oxygen introduced from the outside are combined by the catalyst, and water arises. That is, if it sees with a PEFC simple substance, PEFC will be a very clean energy source which takes out the electrical and electric equipment, when making water from hydrogen and oxygen. Although the hydrogen obtained by a certain method (for example, hydrogen extraction by methanol reforming) is usually used, the hydrogen supplied to a fuel cell, Directly, the direct fuel type fuel cell which introduces methanol etc. into a fuel cell and picks out a proton and an electron from methanol (the indifferent water is used together) according to a catalyst is also being examined briskly.

[0004] Here, a proton conductive film has a duty which tells the proton produced with the anode to the cathode side. Movement of this proton takes place in concertante performance with electron flow as above-mentioned. That is, in PEFC, in order to obtain a high output (namely, high current density), it is necessary to perform proton conduction at sufficient quantity and a high speed. For this reason, it is not an overstatement even if the performance of a proton conductive film calls it the key material which opts for the performance of PEFC. A proton conductive film not only conducts a proton, but has a role of an insulator layer which carries out electric insulation of an anode and a cathode, and a role of a fuel barrier film keep the fuel supplied to the anode side from leaking to the cathode side.

[0005] Now, the main proton conductive films currently used in PEFC are fluoro-resin system films which make perfluoro alkylene a main skeleton and have ion exchange groups, such as a sulfonic group and a carboxylic acid group, at the end of a perfluoro vinyl ether side chain in part. as such a fluoro-resin system film -- for example, a Nafion (R) film (DuPont.) U.S. Pat. No. 4,330,654, a Dow film (DowChemical, JP,4-366137,A), an Aciplex (R) film (Asahi Chemical Industry Co., Ltd., JP,6-342665,A), a Flemion (R) film (Asahi Glass Co., Ltd.), etc. are known.

[0006] From the flume crack which has glass transition temperature ( $T_g$ ) at nearly 130 \*\*, and this temperature neighborhood, since what is called creep happens, the proton conduction structure in a film changes and these fluoro-resin system film cannot demonstrate stable proton conduction performance. In high-temperature-heat Mizushita (for example, not less than 100 \*\*). When arranging a sulfonic group, a carboxylic acid group, etc. on a polymers side chain which is used now and considering it as the proton conductivity grant agent, desorption of a sulfonic group and a carboxylic acid group will take place, and it will replace by the hydroxyl group which hardly has an effect of proton conduction performance grant. The maximum temperature usable stable over a long period of time used now is usually made 80 \*\*

by such reason.

[0007]By the way, since the chemical reaction is used for the fuel cell in the principle, as for energy efficiency, the direction which carries out operating at high temperatures becomes high. That is, considering the same output, the device in which operating at high temperatures is possible can be smaller, and it can make it lightweight. Since the heat can also be used if operating at high temperatures is carried out, what is called cogeneration (cogeneration) becomes possible, and total energy efficiency improves by leaps and bounds. For this reason, the to some extent higher one is made good, and not less than 100 ° of operating temperature of the fuel cell is usually made preferred [ especially not less than 120 ° ].

[0008]When the hydrogen supplied is not fully refined, the catalyst currently used for the anode side may lose activity with the impurity (for example, carbon monoxide) of fuel (what is called catalyst poisoning), and has been a big technical problem which influences the life of PEFC. It is known that it will be avoidable also about this catalyst poisoning if a fuel cell can be operated at an elevated temperature, and it can be said also from this point that it is preferred to carry out operating at high temperatures more as for a fuel cell. If the operation in an elevated temperature is attained, it is not necessary to use the pure article of the precious metals, such as platinum currently used conventionally, it becomes possible to use a metal alloy variously, and the catalyst itself is dramatically advantageous also from the field of cost, or the field of resources.

[0009]Although various examination which extracts a proton and an electron from fuel efficiently directly is performed in the direct fuel type fuel cell now, at low temperature, it is difficult and it is supposed in the elevated temperature (for example, not less than 150 °) that it is possible.

[0010]Thus, since it is to 80 ° as the heat resistance of a proton conductive film is the above-mentioned in spite of supposing that it is preferred to carry out operating at high temperatures more as for PEFC from various fields, the actual condition is that operating temperature is also regulated by 80 °. Moreover, the reaction which occurs during a fuel cell operation is an exoergic reaction.

If it is made to operate, the temperature in PEFC will rise spontaneously.

However, since a proton conductive film has only the heat resistance up to about 80 °, it needs to cool PEFC so that it may not become not less than 80 °. A water cooling system is taken and cooling is usually put into the device of such cooling by the separator portion of PEFC. If such a cooling method is taken, PEFC is large as the whole device, and becomes heavy, and the small size and the feature of being lightweight which are the original features of PEFC cannot fully be employed efficiently. If the operation critical temperature considers it as 80 ° especially, in the simplest water cooling system as a cooling method, effective cooling is difficult. Here, since the quantity of the water used at the time of cooling by being able to cool

effectively that the operation of not less than 100 °C is possible as evaporation heat of water, and also refluxing water can be reduced dramatically, the miniaturization of a device and a weight saving can be attained. In using as an energy source of vehicles especially, if the case where temperature control is carried out at 80 °C is compared with the case where temperature control is carried out above 100 °C, since the capacity of a radiator and cooling water can decrease greatly, PEFC which can operate above 100 °C, i.e., a proton conductive film with the heat resistance of not less than 100 °C, is desired strongly.

[0011]As mentioned above, in spite of desiring an elevated-temperature operation of PEFC, i.e., the elevated-temperature heatproof of a proton conductive film, in respect of versatility, the field of generation efficiency, cogeneration efficiency, and cost and resources, cooling efficiency, etc., the proton conductive film having sufficient proton conductivity, and physical and mechanical properties, such as heat resistance and endurance, does not exist.

[0012]In order to raise the basis of such a background, and the operating temperature of PEFC, the proton conductive material with various heat resistance and endurance is examined and proposed until now. The heat-resistant aromatic system polymer material used as instead of [of the conventional fluorine system film] is typical. For example, polybenzimidazole (JP,9-110982,A), polyether sulphone (JP,10-21943,A, JP,10-45913,A), a polyether ether ketone (JP,9-87510,A), etc. are mentioned. Although these aromatic system polymer materials have the advantage that there are few structural changes at the time of an elevated temperature, there is much what, on the other hand, introduced a direct sulfonic group, a carboxylic acid group, etc. into aromatic series, and in this case, a possibility that remarkable desulfonation and a decarboxylation will happen in an elevated temperature is high, and is not preferred as an elevated-temperature operation film.

[0013]These aromatic system polymer materials do not take ion channel structure etc. like a fluoro-resin system film in many cases. When water exists, there is a tendency for the whole film to swell strongly, and as a result, for change of the film size in this dryness and damp or wet condition, stress is applied to the joined part of a film-electrode conjugate, a possibility that the joined part of a film and an electrode will peel or a film will be torn is high, and there is a problem that membrane failure may happen by the strength reduction of the film by swelling, further. In dryness, since aromatic tendency molecule material is all a very upright high molecular compound, it has the problem that possibilities, such as breakage, are high, in the case of film-electrode conjugate formation.

[0014]On the other hand, the following inorganic materials are also proposed as a proton conductive material. For example, South has obtained the inorganic material of proton conductivity by adding various acid in a hydrolytic silyl compound (SolidStateIonics74 (1994), the 105th page). Although these inorganic materials show proton conductivity stably also at an elevated temperature, when it is considered as a thin film, it is easy to be divided, and there is

a problem that handling and film-electrode conjugate production are difficult. In order to conquer such a problem, the method (JP,8-249923,A) of grinding the inorganic material of proton conductivity, for example, and mixing with an elastomer, the method (JP,10-69817,A) of mixing with sulfonic group content polymers, etc. are tried, but. Since the inorganic bridging body was only mixed for the polymeric material of the binder as for each of these methods, A fundamental thermal property does not have a polymeric-material independent and a big difference, a structural change of a polymeric material takes place in a high temperature region, stable proton conductivity is not shown, and, moreover, in many cases, proton conductivity is not high, either.

[0015]As mentioned above, in order to improve the problem in the conventional polymer electrolyte fuel cell, In spite of having done the research and development about various electrolyte membrane materials, the actual condition was that the proton conductive film which has sufficient endurance and was [ old place ] satisfied with the elevated temperature (for example, not less than 100 \*\*) of the various physical properties of mechanical performance like flexibility does not yet exist.

[0016]

[Problem(s) to be Solved by the Invention]In order that the purpose of this invention may solve the problem in the conventional polymer electrolyte fuel cell, The proton conductivity which was excellent in heat resistance or endurance and was moreover excellent also in the elevated temperature is shown, and it is in providing the proton conductive film with which it was satisfied of the various physical properties of mechanical performance like flexibility, its manufacturing method, and the fuel cell using these proton conductive films.

[0017]

[Means for Solving the Problem]When this invention persons repeat research wholeheartedly about various electrolyte membrane materials in view of an aforementioned problem, as an essential ingredient which constitutes a film, By selecting combination of a specific organic substance, a three-dimensional structure-of-cross-linkage object which has the silicon-oxygen bond combined with it, and a proton conductivity grant agent, It excels in heat resistance and endurance which network structure of a proton conductivity grant agent is formed, and do not look at an example to the former as a result, And proton conductivity excellent also in an elevated temperature is shown, and it finds out that epoch-making organic inorganic composite membrane with which it is satisfied of the various physical properties of mechanical performance like flexibility is obtained, and came to complete this invention.

[0018]Namely, a three-dimensional structure-of-cross-linkage object (A) which has a silicon-oxygen bond according to the invention of the 1st of this invention, Are a carbon atom content structure (B) and a proton conductivity grant agent (C) a proton conductive film to contain, and (i) carbon atom content structure (B), It has a number average molecular weight of 56-30,000,

and has at least four connected carbon atoms in a main chain, and a proton conductive film further characterized by (ii) three-dimensional structure-of-cross-linkage object (A) and a carbon atom content structure (B) being combined by covalent bond is provided.

[0019]According to the invention of the 2nd of this invention, in the 1st invention, a proton conductive film, wherein a three-dimensional structure-of-cross-linkage object (A) and a carbon atom content structure (B) have two or more combination is provided.

[0020]According to the invention of the 3rd of this invention, in the 1st invention, a proton conductive film, wherein a three-dimensional structure-of-cross-linkage object (A) hydrolyzes and condenses simultaneously both sides of 3 organic-functions ARUKOSHI xylan structure and 2 organic-functions ARUKOSHI xylan structure and is formed is provided.

[0021]According to the invention of the 4th of this invention, in the 3rd invention, a proton conductive film, wherein a main skeleton portion of a carbon atom content structure (B) is a hydrocarbon-structures object which consists only of carbon and hydrogen is provided.

[0022]According to the invention of the 5th of this invention, in the 4th invention, a proton conductive film in which a main skeleton portion of a carbon atom content structure (B) is characterized by having the structure shown by the following formula (1) is provided.

[Formula 7]



(n shows the integer of 2-20 among a formula.)

[0023]According to the invention of the 6th of this invention, in the 4th invention, the proton conductive film in which the main skeleton portion of a carbon atom content structure (B) is characterized by having the structure shown by the following formula (2) is provided.

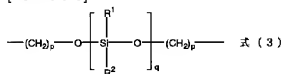
[Formula 8]



(m shows the integer of 0-10 among a formula, and Ar shows the arylene structure of the carbon numbers 6-30.)

[0024]According to the invention of the 7th of this invention, in the 3rd invention, the proton conductive film in which the main skeleton portion of a carbon atom content structure (B) is characterized by having the organic siloxane structure shown by the following formula (3) is provided.

[Formula 9]



(R<sup>1</sup> and R<sup>2</sup> show either a methyl group, an ethyl group or a phenyl group among a formula, p

shows the integer of 0-20, and q shows 20 or less natural number, respectively.)

[0025]According to the invention of the 8th of this invention, in the 1st invention, a proton conductive film, wherein a proton conductivity grant agent (C) is heteropoly acid is provided.

[0026]According to the invention of the 9th of this invention, in the 8th invention, the proton conductive film according to claim 8, wherein heteropoly acid is either tungstophosphoric acid, molybdophosphoric acid or tongue strike silicic acid is provided.

[0027]According to the invention of the 10th of this invention, in the 1st invention a proton conductivity grant agent (C), as opposed to total quantity 100 weight section of a three-dimensional structure-of-cross-linkage object (A) and a carbon atom content structure (B) -- 10 - 300 weight-section \*\*\*\* -- the proton conductive film according to claim 1 characterized by things is provided.

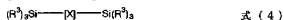
[0028]The carbon atom content structure constituent (D) which, on the other hand, has two or more hydrolytic silyl groups according to the invention of the 11th of this invention, The 1st process of preparing the mixture containing a proton conductivity grant agent (C), The 2nd process of producing the prepared this mixture by arbitrary means, and the hydrolytic silyl group contained in the this produced mixture are hydrolyzed, Either of the 1-10th inventions including the 3rd process of forming a three-dimensional structure-of-cross-linkage object (A) is provided with the manufacturing method of the proton conductive film of a statement by making it condense.

[0029]A carbon atom content structure constituent (D) which has two or more hydrolytic silyl groups in the 11th invention according to the 12th invention of this invention, A manufacturing method of a proton conductive film containing a compound (E) which has two or more 3 organic-functions hydrolytic silyl groups, and every at least one or more compounds (F) which have two or more 2 organic-functions hydrolytic silyl groups is provided.

[0030]A carbon atom content structure constituent (D) which has two or more hydrolytic silyl groups in the 11th invention according to the 13th invention of this invention, A manufacturing method of the proton conductive film containing a compound (G) which has both a 3 organic-functions hydrolytic silyl group and one or more 2 organic-functions hydrolytic silyl groups according to claim 11 is provided.

[0031]According to the invention of the 14th of this invention, in the 12th invention, a manufacturing method of a proton conductive film, wherein a compound (E) which has two or more 3 organic-functions hydrolytic silyl groups is a compound expressed with the following formula (4) is provided.

[Formula 10]

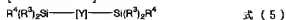


(Among a formula,  $R^3$  is either a methoxy group, an ethoxy basis, a phenoxy group or chlorine,

and X shows structure of a formula (1) mentioned above, a formula (2), or a formula (3).)

[0032]According to the invention of the 15th of this invention, in the 12th invention, a manufacturing method of a proton conductive film, wherein a compound (F) which has two or more 2 organic-functions hydrolytic silyl groups is a compound expressed with the following formula (5) is provided.

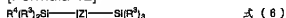
[Formula 11]



(Among a formula, either a methoxy group, an ethoxy basis, a phenoxy group or chlorine and  $R^4$  are either a methyl group, an ethyl group or a phenyl group, and, as for Y,  $R^3$  shows the structure of the formula (1) mentioned above, a formula (2), or a formula (3).)

[0033]According to the invention of the 16th of this invention, in the 13th invention, the manufacturing method of a proton conductive film, wherein the compound (G) which has both a 3 organic-functions hydrolytic silyl group and one or more 2 organic-functions hydrolytic silyl groups is a compound expressed with the following formula (6) is provided.

[Formula 12]



(Among a formula, either a methoxy group, an ethoxy basis, a phenoxy group or chlorine and  $R^4$  are either a methyl group, an ethyl group or a phenyl group, and, as for Z,  $R^3$  shows the structure of the formula (1) mentioned above, a formula (2), or a formula (3).)

[0034]According to the invention of the 17th of this invention, in the 11th invention, in order to make the efficiency of the 3rd process increase, the manufacturing method of the proton conductive film making water (H) contain in a mixture at the 1st process beforehand is provided.

[0035]According to the invention of the 18th of this invention, in the 11th invention, the manufacturing method of the proton conductive film according to claim 11 performing further the process aged at 100-300 \*\* following on the 1st - the 3rd process is provided.

[0036]According to the invention of the 19th of this invention, the fuel cell which uses the proton conductive film of a statement for either of the 1-10th inventions is provided.

[0037]

[Embodiment of the Invention]Hereafter, this invention is explained in detail.

[0038]The proton conductive film of this invention contains the three-dimensional structure-of-cross-linkage object (A) and (A), the carbon atom content structure (B) which carried out the covalent bond, and a proton conductivity grant agent (C) as an essential ingredient which constitutes a film.

[0039]Then, on account of explanation, although a full account is given one by one about above-mentioned (A) - (C), if a carbon atom content structure (B) is explained first, a carbon

atom content structure (B) needs to have a three-dimensional structure-of-cross-linkage object (A) and one or more covalent bonds. Here, unless it has combination at all, these hydrocarbon compounds have a gas, a liquid state, or the shape of paraffin dissolved at an elevated temperature, and are not realized as a proton conductive film used at an elevated temperature. As for bridge construction, only just one is [ combination with (A) ] insufficient, and as for the intensity of sufficient film, since it is not obtained but phase separation structure moreover also collapses easily, it is preferred to have two or more combination. Acquisition of material is difficult for what, on the other hand, has three or more combination, and since crosslinking density goes up, it becomes hard and pliability is spoiled, as a bonding number, two is preferred.

[0040] However, when combination with (A) fully has two or more (B), as long as it can secure membranous pliability and conduction stability, the carbon atom inclusion which has not been combined with (A), the thing combined with (A) one time, or the thing united three or more may be contained. Since the minimum content of (B) whose bonding number with (A) is 2 in that case is based also on the chain length of (B), it cannot generally be said, but it is usually not less than 50%.

[0041] When the bonding number of (A) and (B) uses saturated hydrocarbon as a main skeleton portion by 2, the compound represented by a following formula (1) and formula (2) is preferred. The organic siloxane expressed with the following formula (3) is also mentioned as a structure of fulfilling membranous various physical properties.

[0042]

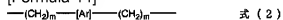
[Formula 13]



(n shows the integer of 2-20 among a formula.)

[0043]

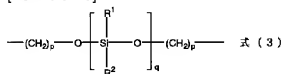
[Formula 14]



(m shows the integer of 0-10 among a formula, and Ar shows the arylene structure of the carbon numbers 6-30.)

[0044]

[Formula 15]



(R<sup>1</sup> and R<sup>2</sup> show either a methyl group, an ethyl group or a phenyl group among a formula, p

shows the integer of 0-20, and q shows 20 or less natural number, respectively.)

[0045]A compound of the above-mentioned formula (1) is combined with a three-dimensional structure-of-cross-linkage object (A) at both ends of a methylene chain. Here, although 2-20 are preferred as for several n of a methylene chain, 4-14 are used especially preferably. If a film becomes weak in 1 and n increases more than 20 on the other hand, an effect of improvement in heat-resistant with a three-dimensional structure-of-cross-linkage object (A) will decrease. A compound represented by formula (2) on the other hand when a bonding number of (A) and (B) uses unsaturated hydrocarbon as a main skeleton portion by 2 is preferred. The paraffin, for example, methane, which has the chain structure of CH<sub>2</sub> as an example. Ethane, propane, butane, pentane, hexane, heptane, octane, A thing of straight chain shape, such as nonane, Decane, an undecane, a dodecane, a tridecane, tetradecane, pentadecane, hexadecane, heptadecane, octadecane, nonadecane, and an eicosane, its isomer, or a branched thing is mentioned.

[0046]A compound of the above-mentioned formula (2) has the arylene structure containing an aromatic ring, may have alkylene structure into a portion connected with a three-dimensional structure-of-cross-linkage object (A), and may couple it directly with it (m= 0). (although 1-10 are preferred as for m, 1-especially 6 are preferred) Here, replacement positions in particular to an aromatic ring may not have limitation, alt.\*\* meta, Para, and any may be sufficient as them, and a mixture may be sufficient as them. As an example of arylene structure, benzene, biphenyl, terphenyl, Quarter phenyl or a naphthalene derivative, an anthracene derivative, a pyrene derivative, an acenaphthylene derivative, a fluorene derivative, a phenanthrene derivative, perylene derivatives, these substitution products, etc. are mentioned.

[0047]As an example of representation of a main skeleton portion of a carbon atom content structure (B), A compound of the above-mentioned formula (3) was mentioned, and in this compound, it couples directly with a three-dimensional structure-of-cross-linkage object (A) by siloxane bond both ends, or (p= 0) has joined together via alkylene structure (although 1-10 are preferred as for p, 1-especially 6 are preferred). Here, although 2-20 are preferred as for several q of a siloxane chain, 6-10 are used especially preferably. If q increases more than 20, an effect of improvement in heat-resistant with a three-dimensional structure-of-cross-linkage object (A) will decrease. Specifically, structures which repeat dimethylsiloxane, a diethyl siloxane, a JIFENIRURU siloxane, an ethylmethyl siloxane, a methylphenyl siloxane, and an ethylphenyl siloxane, or those BURROKU connected structure are mentioned.

[0048]This carbon atom content structure (B) gives moderate pliability to a proton conductive film, and it is used in order to make easy handling by a film independent, and creation of a film-electrode conjugate. By adjusting compatibility with a proton conductivity grant agent (C), an island and (C) make it take phase separation structure of the shape of a sea island used as the sea, and, simultaneously with it, (B) realizes high conductivity. For the former, as for (B), since

crosslinking density is adjusted by chain length of (B), it is preferred to have moderate length. Since moderate length said here is influenced by branching of a chain, the flexibility of combination, existence of a ring structure, etc., it cannot be limited, but in carbon-carbon methylene chain combination, one to about 50 are preferred, and especially its combination of 4-20 is preferred. In order to become a weak film, and to close an ion conduction course on the other hand if too long although it is usable when a carbon to carbon bond is one to about three, conductivity falls and it is not desirable.

[0049]Next, if a proton conductivity grant agent (C) is explained, a proton conductivity grant agent (C) of this invention bears a duty which raises proton concentration in a proton conductive film, but. In view of proton conductivity being proportional to concentration of a medium (water usually supplied separately) which transmits concentration of a proton, and a proton, when a rise of proton concentration realizes high proton conductivity of this invention, it is indispensable.

[0050]As a proton conductivity grant agent (C), what is called an acid compound that emits a proton is used. Here, as a kind of acid compound added as a proton conductivity grant agent, phosphoric acid, sulfuric acid, sulfonic acid, carboxylic acid, boric acid, heteropoly acid, those derivatives, etc. are mentioned. In this invention, two or more sorts of of these acid or its derivative may be used together. Also in these, it is preferred to use heteropoly acid. Here, heteropoly acid refers to inorganic oxo acid, and what has Keggin structure of tungstophosphoric acid, molybdophosphoric acid, tongue strike silicic acid, etc. and the Dawson structure also in it is used preferably.

[0051]These heteropoly acid has large molecular size enough, and elution of acid from a film is considerably controlled also under existence of water etc. Heteropoly acid has ion polarity and hydrogen bond power, and as mentioned above, Since it becomes possible to be held in a film by polar interaction with a silicon-oxygen bond, and to prevent elution of acid at the same time phase separation with a carbon atom content compound (B) happens efficiently and conductivity increases, In a proton conductive film used at an elevated temperature over a long period of time, it can use preferably especially. If acidity is large and molecular size and a size of polar interaction with a metal-oxygen bond are taken into consideration also in inorganic solid acid, tungstophosphoric acid, molybdophosphoric acid, and tongue strike silicic acid will be used especially preferably. In this invention, these heteropoly acid and other acid may be used together as a proton conductivity grant agent (C), and, in addition to this, two or more organic acid and inorganic acid may be used together.

[0052]As a proton conductive film of this invention was mentioned above, use as an essential ingredient a carbon atom content structure (B) and a proton conductivity grant agent (C) which carried out the covalent bond to the three-dimensional structure-of-cross-linkage object (A) and (A), but. among these -- a proton conductivity grant agent (C) receives total quantity 100

weight section of a three-dimensional structure-of-cross-linkage object (A) and a carbon atom content structure (B) -- 10 - 300 weight-section \*\*\*\* -- it is characterized by things. If a proton conductivity grant agent (C) is ten or less weight sections to total quantity 100 weight section of a three-dimensional structure-of-cross-linkage object (A) and a carbon atom content structure (B), Since it becomes impossible for sufficient conductivity not to be expectable, to secure a film property on the other hand if more than 300 weight sections, and for a proton conductivity grant agent (C) to hold enough by three-dimensional structure-of-cross-linkage object (A) and a carbon atom content structure (B), loss out of a film of a proton conductivity grant agent (C) takes place.

[0053]Although a proton conductive film of this invention uses as an essential ingredient a carbon atom content structure (B) and a proton conductivity grant agent (C) which carried out the covalent bond to the three-dimensional structure-of-cross-linkage object (A) and (A), Other optional components, such as a reinforcing agent, a softening agent, a surface-active agent, a dispersing agent, a reaction accelerator, stabilizer, colorant, an antioxidant, inorganic matter, or an organic bulking agent, can be added within limits which do not spoil the purpose of this invention besides it.

[0054]A proton conductive film of this invention is producible with some manufacturing methods stated to the following 1-3, for example.

1) A carbon atom content structure constituent (D) which has a substituent (for example, hydrolytic silyl compound) which forms a three-dimensional structure-of-cross-linkage object (A) which consists of a silicon-oxygen bond one or more, The first process of preparing a mixture which mixed a proton conductivity grant agent (C), A substituent (for example, hydrolytic silyl compound) which forms a three-dimensional structure-of-cross-linkage object (A) which consists of a silicon-oxygen bond included in the second process of producing it by a publicly known means, and produced material is hydrolyzed, what is called sol that forms a three-dimensional structure-of-cross-linkage object (A) by a condensation reaction -- a method of forming a three-dimensional structure-of-cross-linkage object (A) by passing through the third process of performing a gel (sol-gel) reaction, and obtaining the target proton conductive film.

2) A substituent which forms a three-dimensional structure-of-cross-linkage object (A) which consists of a silicon-oxygen bond. After preparing the system of reaction containing a carbon atom content structure constituent (D) which has (for example, a hydrolytic silyl compound) and producing it by a publicly known means, by making a steam or water exist, sol -- a method of obtaining the target proton conductive film by performing a gel (sol-gel) reaction, forming a three-dimensional structure-of-cross-linkage object (A), contacting a film produced by making it such, and a solution containing a proton conductivity grant agent (C), and introducing a proton conductivity grant agent (C) into a film.

3) a basis (for example, unsaturated bonds, such as a vinyl group,) in which a carbon atom content compound (B) and a covalent bond are possible A three-dimensional structure-of-cross-linkage object (A) which consists of a silicon-oxygen bond which has a functional group in which covalent bonds, such as a hydroxyl group, an amino group, and an isocyanate group, are possible is formed in the shape of a film, How to obtain the target proton conductive film by impregnating this with a carbon atom content compound and a proton conductivity grant agent (C) which have a substituent reacted to a basis in which the above-mentioned covalent bond is possible, and making a covalent bond form in (A) and (B).

[0055]Although not limited for a process of this invention to the above-mentioned manufacturing method at all, said especially method of 1 is preferred from fields, such as simplicity of operation, reliability, and a manufacturing facility, also in these.

[0056]Next, in order to give a full account further about a manufacturing method of a proton conductive film of this invention, said method of 1 is explained along with order of each process. In a suitable manufacturing method of a proton conductivity grant agent of this invention, the first process of preparing a carbon atom content structure constituent (D) which has one or more hydrolytic silyl groups, and a mixture containing a proton conductivity grant agent (C) is included.

[0057]As a substituent which forms here a three-dimensional structure-of-cross-linkage object (A) which consists of a silicon-oxygen bond, a hydrolytic silyl group is preferred. As a hydrolytic silyl group, for example Trimethoxysilane, triethoxysilane, Trialkoxysilane, such as a triisopropoxy silane and triphenoxysilane. Tri halogenation Silane, such as trichlorosilane, methyldiethoxysilane, Methyl dimethoxysilane, ethyldiethoxysilane, ethyl dimethoxysilane, Dialkoxy one or dihalogen-ized silyl groups, such as methyldi chlorosilane and ethyldichlorosilane, Monoalkoxy \*\*\*\*, such as a dimethylethoxy silane, dimethyl methoxysilane, and dimethylchlorosilane, can use a mono- halogenation silyl group or a hydroxy silyl group. Various compounds are marketed, it is easily and cheaply available, and these hydrolytic silyl group is easy to control a sol-gel reaction which forms a three-dimensional bridging body which consists of a silicon-oxygen bond.

[0058]Hydrolytic metallic compounds which give these other metallic oxides, such as titanium, a zirconium, and aluminum, in that case, For example, a carbon atom content compound containing substituents, such as a complex with an alkoxide (mono- \*\* JI, Tri) of titanium, a zirconium, and aluminum or an acetylacetone, may be added. As for hydrolytic metallic compounds other than these silicon, although there is no restriction in an addition, it is preferred to consider it as an addition not more than 50mol% from the ease of cost or reaction control to a hydrolytic silyl group.

[0059]A hydrolytic inorganic compound may be added as a precursor of a three-dimensional structure-of-cross-linkage object which becomes these from a metal-oxygen bond which does

not have a carbon atom content compound (D) and combination. As such a hydrolytic inorganic compound, for example A tetraethoxysilane, A tetramethoxy silane, tetra-isopropoxysilane, tetra-n-butoxysilane, tetra-t-butoxysilane, Or alkoxy silicate, such as monoalkyl one of these and dialkyl, Phenyltriethoxysilane, halogenation Silang, tetraethoxytitanium, tetra-isopropoxy titanium, tetra-n-butoxytitanium, tetra-t-butoxytitanium, Or alkoxy titanate containing crosslinking reaction speed-control group substitution products, such as monoalkyl one of these, a dialkyl object, and an acetylacetone, the oligomer, alkoxy zirconate, etc. are mentioned. As for an addition ratio of a carbon atom content structure constituent (D) and hydrolytic metallic compounds which do not have combination, it is desirable to use less than 30mol% to a carbon atom content structure constituent (D) which has one or more hydrolytic silyl groups. If it carries out more than 30mol%, phase separation structure of a carbon atom containing phase and a mineral phase becomes indefinite, and high proton conductivity cannot be demonstrated.